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R. Gans

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ON THE SHAPE OF ULTRAMICROSCOPIC GOLD PARTICLES

by

R. Gans*

1. Introduction

After much discussion of the phenomenon, the color appearances of metals in the colloidal state have been very elegantly clarified in a theoretical study by Mie[1] and in an experimental investigation by his erstwhile student, Steubing[2].

These treatises show that the optical constants of the metal concerned and the particle size are the color-determining factors, but that a resonance phenomenon is out of the question, contrary to prior speculations.

In the referenced paper, Mie calculated the absorption curves for colloidal gold solutions, with the assumption that the particles were spheres whose refractive index and absorption coefficient possessed the same values, for individual wavelengths, as those for metallic gold, from the measurement of Hagen and Rubens.

The consequence of this assumption[3] is that very small gold particles give ruby-red solutions and that with increasing particle size, these solutions first take on a tinge of blue, then violet, deep blue, indigo blue, and finally greenish blue.

Mie's treatment still contains one small deficiency, of which he himself was surely aware, namely that his theoretical investigation took only spheres

*Strassburg

into account, for which there is no further reason, a priori, than analytical simplicity.

It thus developed that certain empirical observations of Steubing, e.g. blue gold solutions with very small particle size or the occurrence of natural light from the diffractive deflection of linearly polarized light by the particles, could not be explained by the Mie theory.

On the one hand, to fill this gap, I undertook the present investigation; on the other hand, it follows from the agreement between Mie's theory and Steubing's experiments only that the particles may be spheres, not that they must be. The desire to decide this issue also stimulated me to attack the problem, since I felt it was important that it be possible, in special cases even for ultramicroscopic objects, to obtain information on their form, if only indirectly.

It seemed simplest to stipulate that the particles be ellipsoids. By controlling the axis ratio, it is then possible to treat all types of shapes from the disk to the rod, including the sphere itself.

Of course, in purely mathematical terms, the thus modified task is incomparably more difficult than for the assumption of spherical particles; I have not solved it to the same degree of generality as Mie did for spheres, but rather have restricted myself to particles whose linear dimensions are small compared to the wavelengths of the light.

That I specialized the solution even further by assuming ellipsoids of rotation would not have been absolutely necessary, but was desirable in order to minimize the scope of the numerical calculations. Without these restrictions, incidentally, there would have been hardly any difference in the physical results of the investigation.

The results can be summarized as follows. The appearance of the absorption curves depends very strongly on the particle shape, so that one must conclude from Steubing's spectrophotometric observations on ruby-red solutions: The particles can certainly not deviate much from the spherical shape. And from his polarization observations: The particles must deviate a little from the spherical shape.

2. The Electromagnetic Field of an Ellipsoid Impinged upon by a Plane Light Wave

In an infinitely extended quantity of water, let there be an ellipsoid of rotation of gold, whose linear dimensions are small compared to the wavelength of light. Let a plane, linearly polarized wave of amplitude 1 and of vibration number n impinge upon this ellipsoid.

A perturbation of the electromagnetic field is then caused by the gold particle; with the just-mentioned assumption that the particle is small compared to the wavelength, this perturbation can easily be stated using an artifice due to Lord Rayleigh[4].

This artifice consists of regarding the electric field in the interior of the ellipsoid as quasi-static. In order to calculate it, we thus have to solve the well-known problem of introducing an ellipsoid of rotation of dielectric constant m^2 into a medium of dielectric constant m_0^2 in which there is a uniform electric field $\mathfrak{E}_0$.

If we make the center of the ellipsoid the origin of a coordinate system ξ, η, ζ, whose ξ-axis lies in the direction of the body axis of the ellipsoid, then the electric field in the interior of the ellipsoid is given by[5]:

$$\mathfrak{E}_\xi = \frac{\mathfrak{E}_{\xi 0}}{1 + \frac{m'^2 - 1}{4\pi} P}$$

$$\mathfrak{E}_\eta = \frac{\mathfrak{E}_{\eta 0}}{1 + \frac{m'^2 - 1}{4\pi} P'} \qquad (1)$$

$$\mathfrak{E}_\zeta = \frac{\mathfrak{E}_{\zeta 0}}{1 + \frac{m'^2 - 1}{4\pi} P''}$$

where

$$m'^2 = \frac{m^2}{m_0^2} \tag{2}$$

denotes the ratio of the dielectric constant of the ellipsoid to that of the environment.

Furthermore, P is a quantity which depends only on the axis ratio of the ellipsoid; for prolate ellipsoids it has the value

$$P = 4\pi \frac{1-e^2}{e^2}\left(\frac{1}{2e}\lg\frac{1+e}{1-e} - 1\right) \tag{3}$$

and for oblate ellipsoids, the value

$$P = \frac{4\pi}{e^2}\left(1 - \frac{\sqrt{1-e^2}}{e}\arcsin e\right) \tag{4}$$

where e signifies the numerical eccentricity of the meridian ellipse with semiaxes A and B. Thus:

$$e = \frac{\sqrt{A^2 - B^2}}{A} \tag{5}$$

P' is obtained from P by the relation

$$P + 2P' = 4\pi \tag{6}$$

From the field strength $\mathfrak{E}$ we obtain the polarization, i.e. the induced electric moment per unit volume of the ellipsoid, from the equation

$$\mathfrak{P} = \frac{m^2 - m_0^2}{4\pi}\mathfrak{E} = m_0^2\frac{m'^2-1}{4\pi}\mathfrak{E} \tag{7}$$

so that the ellipsoid of volume V represents an electric moment of magnitude

$$\mathfrak{f} = \mathfrak{P}V = m_0^2\frac{m'^2-1}{4\pi}V\mathfrak{E} \tag{8}$$

This can be written with the help of equation (1):

$$\begin{aligned}
\mathfrak{f}_\xi &= m_0^2\frac{m'^2-1}{4\pi + (m'^2-1)P}V\mathfrak{E}_{0\xi} = g\,\mathfrak{E}_{0\xi} \\
\mathfrak{f}_\eta &= m_0^2\frac{m'^2-1}{4\pi + (m'^2-1)P'}V\mathfrak{E}_{0\eta} = g'\,\mathfrak{E}_{0\eta} \\
\mathfrak{f}_\zeta &= m_0^2\frac{m'^2-1}{4\pi + (m'^2-1)P'}V\mathfrak{E}_{0\zeta} = g'\,\mathfrak{E}_{0\zeta}
\end{aligned} \tag{9}$$

or, if we multiply the numerator and denominator by $3/4\pi$:

$$\mathfrak{f}_\xi = m_0^2\frac{m'^2-1}{3 + (m'^2-1)\frac{3}{4\pi}P}\frac{3}{4\pi}V\cdot\mathfrak{E}_{0\xi} = g\,\mathfrak{E}_{0\xi} \quad \text{etc.} \tag{10}$$

Here g and g' are readily understandable abbreviations.

In our optical problem, m' is the ratio of the refractive index of gold to that of water; the former is complex due to the absorption by the gold, and the latter is taken to be real (we thus neglect light absorption by the water).

Knowledge of the electric moment of an ellipsoid suffices to determine the absorption curve of a colloidal gold solution and the polarization conditions which obtain therein.

If we also wish to know the field external to the ellipsoid, namely at distances which are large compared to the semiaxes, we can calculate it simply by superposition of the fields of Hertzian dipoles with the moments f_ξ, f_η, and f_ζ, according to well-known formulas[6].

3. The Absorption

To continue, we assume a fixed coordinate system x, y, z in the solution. Let the plane wave propagate in the x-direction and be polarized in the xy-plane, i.e. let only $\mathfrak{E}_{0z}$ be different from zero.

Let
$$\mathfrak{E}_{0z} = e^{2\pi i\left(nt - \frac{x}{\lambda'}\right)} \tag{11}$$

where λ' is the wavelength of the light in water.

If the direction cosines of the ξ, η, ζ-axes toward the x, y, z-axes are characterized by the scheme

	x	y	z
ξ	α_1	α_2	α_3
η	β_1	β_2	β_3
ζ	γ_1	γ_2	γ_3

then
$$\mathfrak{E}_{0\xi} = \alpha_3 \mathfrak{E}_{0z}; \quad \mathfrak{E}_{0\eta} = \beta_3 \mathfrak{E}_{0z}; \quad \mathfrak{E}_{0\zeta} = \gamma_3 \mathfrak{E}_{0z} \tag{12}$$

and, from equation (10):

$$\begin{aligned} f_\xi &= g\,\alpha_3\,\mathfrak{E}_{0z} \\ f_\eta &= g'\beta_3\,\mathfrak{E}_{0z} \\ f_\zeta &= g'\gamma_3\,\mathfrak{E}_{0z} \end{aligned} \tag{13}$$

Through multiplication of the three equations (13) by α_3, β_3, and γ_3, respectively, and addition, we obtain

$$f_z = \{g\,\alpha_3^2 + g'(\beta_3^2 + \gamma_3^2)\} \cdot \mathfrak{E}_{0z} \tag{14}$$

or, using one of the relations between the direction cosines:

$$f_z = \{(g - g')\alpha_3^2 + g'\}\,\mathfrak{E}_{0z} \tag{15}$$

If the axis directions of the ellipsoids are distributed at random, then the mean value of α_3^2 becomes 1/3, and thus the mean value $\overline{f}_z$ of f_z becomes

$$\overline{f}_z = (\tfrac{1}{3}g + \tfrac{2}{3}g')\,\mathfrak{E}_{0z} = \bar{g}\,\mathfrak{E}_{0z} \tag{16}$$

while $\overline{f}_x = \overline{f}_y = 0$.

To calculate the mean moment, which is of concern for the absorption alone, we can thus assume, from equation (16), that the body axes of one third each of all of the particles are parallel to the three coordinate axes x, y, z.

Now the absorption per unit length is given by[7]:

$$k = \frac{4\pi N}{m_0^2}\,\frac{2\pi}{\lambda'}\,\mathfrak{Im}(-\bar{g}) \tag{17}$$

or, using the values of g and g' from equation (10)

$$k = NV\,\frac{6\pi}{\lambda'}\,\mathfrak{Im}\left(-\frac{a_1}{3} - \frac{2}{3}a_1'\right) \tag{18}$$

if we make use of Mie's notation:

$$a_1 = \frac{m'^2 - 1}{3 + (m'^2 - 1)\frac{3}{4\pi}P} \qquad a_1' = \frac{m'^2 - 1}{3 + (m'^2 - 1)\frac{3}{4\pi}P'} \tag{19}$$

NV is the total gold volume per unit volume of solution. The absorption is proportional to this.

Finally, if we let

$$k = K \cdot NV \tag{20}$$

then K denotes the absorption calculated on the basis of unit volume concentration, and its value is

$$K = \frac{6\pi}{\lambda'} \Im m\left(-\tfrac{1}{3}a_1 - \tfrac{2}{3}a_1'\right) = \tfrac{1}{3}U_P + \tfrac{2}{3}U_P; \tag{21}$$

if U_P is the abbreviation for

$$U_P = \frac{6\pi}{\lambda'} \Im m(-a_1) \tag{21'}$$

For spheres, P = P' = 4π/3, and thus, from equation (19), $a_1 = a_1' = m'^2 - 1/m'^2 + 2$; equation (21) thus transforms to the equation found by Mie.

4. The Absorption Curves

From the observations of Hagen and Rubens on the reflectivity and absorptivity of gold, Mie calculated m'^2 for various wavelengths. He found:

Table 1.

λ	λ'	m'^2
420	313	0,00 − i 3,20
450	336	− 0,017 − i 3,32
500	374	− 1,60 − i 2,49
525	393	− 2,45 − i 1,98
550	412	− 3,20 − i 1,57
600	450	− 4,84 − i 1,26
650	487	− 6,97 − i 1,63

In this table, λ and λ' denote the wavelengths in air and water, respectively.

With these values, and taking the values for P and P' from equations (3) to (6), I used equation (21') to calculate the quantity U_P for various values of P; from that, using equation (21), I calculated K for various shapes of prolate and oblate ellipsoids of rotation.

The results are given in the following tables.

Table 2. The quantity U_p.

$\frac{3}{4\pi}P = 0$	0,2	0,4	0,5	0,6	0,8	1,0	1,1	1,2
$\lambda = 420$	64,26	70,09	68,84	65,63	61,20	50,77	40,6	36,14	32,14
450	62,10	67,66	65,90	62,30	57,80	47,06	37,4	33,17	29,27
500	41,83	58,82	57,38	84,59	87,74	78,27	59,2	49,99	42,06
525	31,66	51,80	60,49	109,1	124,9	111,2	69,1	52,85	40,81
550	23,94	45,18	64,33	151,7	193,5	125,3	55,2	38,27	27,73
600	17,60	46,30	114,8	392,2	189,0	41,56	16,4	11,57	8,62
650	21,04	90,57	402,7	116,1	45,84	14,44	6,92	5,18	4,01

$\frac{3}{4\pi}P = 1,25$	1,3	1,4	1,5	1,8	2,0	2,2	2,6	3,0
$\lambda = 420$	30,34	28,51	25,55	22,87	16,70	13,78	11.52	8,29	6,27
450	27,43	26,02	23,16	20,72	15,10	12,41	10,38	7,47	5,63
500	38,69	35,38	30,07	25,43	16,44	12,70	10,06	6,71	4,77
525	36,11	32,08	25,85	21,00	12,41	9,22	7,09	4,57	3,18
550	24,15	21,00	16,41	13,09	7,52	5,52	4,22	2,70	1,88
600	7,52	6,64	5,31	4,31	2,58	1,94	1,51	0,99	0,70
650	3,59	3,25	2,65	2,20	1,38	1,06	0,84	0,57	0,41

I. Prolate Ellipsoids of Rotation

Table 3.

Nr.	$\frac{B}{A}$	$\frac{3}{4\pi}P$
1	1,00	1,0
2	0,77	0,8
3	0,57	0,6
4	0,48	0,5
5	0,40	0,4
6	0,23	0,2
7	0,00	0,0

Table 4. The quantity K.

λ	Nr. 1	2	3	4	5	6	7
420	40,6	41,0	41,8	42,1	42,0	40,4	36,7
450	37,4	37,8	38,8	39,1	39,3	38,0	34,5
500	59,2	59,4	57,3	54,0	42,7	39,7	30,9
525	69,1	72,3	68,8	60,5	41,5	34,5	24,5
550	55,2	67,3	83,0	66,7	35,4	26,0	16,7
600	16,4	21,6	68,7	136,0	42,7	19,0	8,7
650	6,92	8,3	18,0	41,1	136,4	32,0	8,5

Table 3 contains: in the first column, sequential numbers for each particle shape; in the second column, the axis ratio of the meridian ellipse; in the third column, the quantity $3/(4\pi)P$, which is taken into account for fields in the direction of the body axis.

Solution No. 1, e.g., contains the gold in spherical form (B/A = 1); solution No. 7, in rod form (B/A = 0).

In order to make the shapes of the particles directly evident, I prepared Figure 1, in which, although I did not construct the meridian ellipses precisely, I did draw them with the proper axis ratio and with the body axis marked.

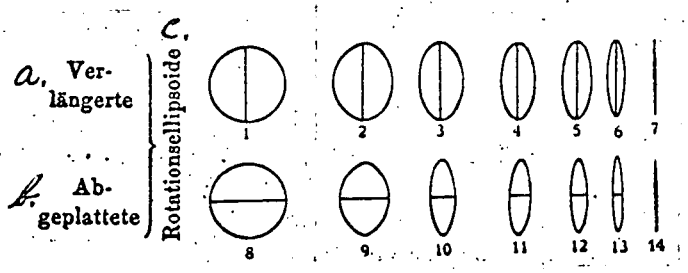

Fig. 1.

Key: a. prolate
b. oblate
c. ellipsoids of rotation

Table 4 contains the absorptions for the wavelengths (in air) indicated in the first column; the numbers signify the light loss in a 1 mm path through a solution of concentration $NV = 10^{-6}$ (i.e. 1 mm^3 of gold in 1 ℓ of water), in per mill.

The absorption curves calculated thus are shown graphically in Figure 2.

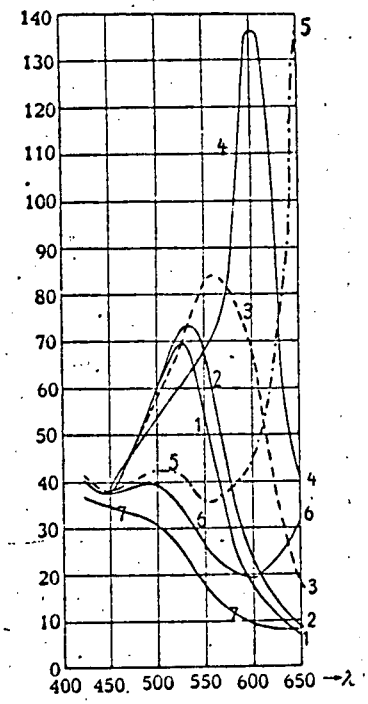

Fig. 2. Prolate ellipsoids of rotation.

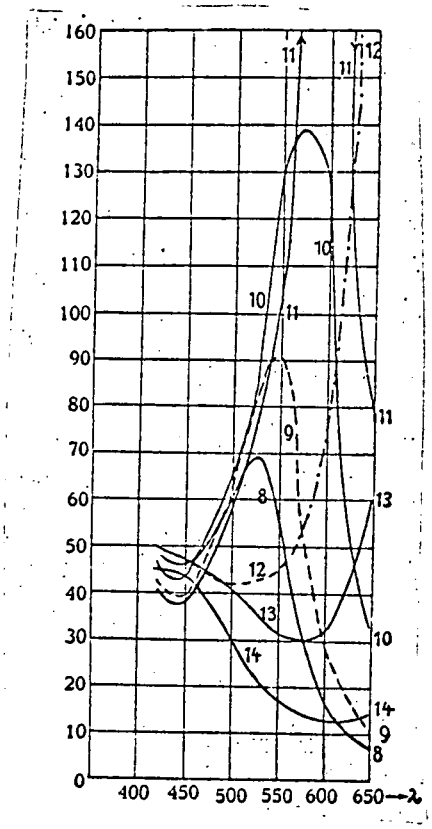

Fig. 3. Oblate ellipsoids of rotation.

II. Oblate Ellipsoids of Rotation

Table 5.

Nr.	$\frac{B}{A}$	$\frac{3}{4\pi} P'$
8	1,00	1,0
9	0,62	0,8
10	0,38	0,6
11	0,29	0,5
12	0,22	0,4
13	0,10	0,2
14	0,00	0,0

Table 6. The quantity K.

λ	Nr. 8	9	10	11	12	13	14
420	40,6	42,4	46,4	48,3	49,7	49,5	44,9
450	37,4	39,1	43,6	45,7	47,4	47,6	43,3
500	59,2	62,2	64,0	60,6	41,6	41,4	29,5
525	69,1	82,7	87,4	75,8	42,7	36,0	22,2
550	55,2	89,0	131,5	102,9	44,3	31,0	16,6
600	16,4	29,5	126,9	262,5	77,0	31,2	12,0
650	6,92	10,5	31,0	77,7	268,8	60,6	14,2

Table 5 corresponds to Table 3. Solution No. 8, e.g., contains spheres, solution No. 14, plates. The meridian ellipses with properly drawn axis ratios are shown in the lower row of Figure 1.

Table 6 corresponds to Table 4, representing the absorption curves which are shown graphically in Figure 3.

The strong dependence of the absorption curves on the particle shape is noticeable at first glance. Whereas the absorption maximum for spheres is in the green, thus giving ruby-red solutions, it immediately shifts, for both prolate and oblate particles, to longer wavelengths and becomes significantly higher, accordingly giving rise to blue solutions.

If we compare the absorption curves obtained by Steubing from three red solutions (Figure 4) with those which we have calculated, we can draw the conclusion that *the gold particles in these solutions are certainly nearly spherical.**

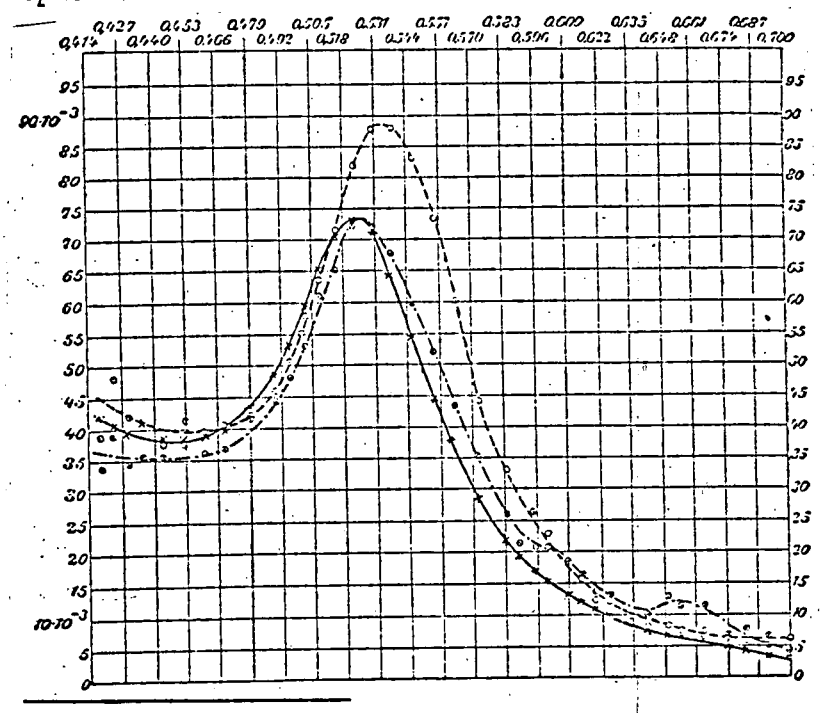

Fig. 4. The three red solutions.

Solution B, A, C — Absorption.

*This statement is, of course, to be taken with a grain of salt, since we have only compared spheres with ellipsoids. It is conceivable that the gold particles could be present in the form of octahedra. What we can say, however, is that no one direction in the particle can be particularly favored in terms of its length.

On the other hand, we see that even very small particles can yield blue solutions, which did not follow from Mie's theory but which corresponds to empirical observations (cf. W. Steubing, Dissertation, p. 38), namely when the particles are prolate or oblate.

In examining absorption curve No. 14 from Figure 3, which holds for circular plate-shaped particles, it appears quite out of the question that intensely red gold-containing glasses with very small particles could have the lamellar shape, which Siedentopf and Zsigmondy[8] regard as being not impossible.

5. The Color of the Gold Particles

For the radiation from a particle impinged upon by a linearly polarized light wave of amplitude 1, whose electric vector oscillates parallel to one of the principal axes of the ellipsoid, we obtain

$$F = \frac{24\pi^3 V^2}{\lambda^4} \frac{|m'^2 - 1|^2}{\left|3 + (m'^2 - 1)\frac{3}{4\pi} P\right|^2} \tag{21a}$$

if P denotes the de-electrification coefficient for the corresponding axis direction.

Proportional to this radiation is the light intensity observed when the direction of vision is perpendicular to the incident beam but parallel to its plane of polarization.*

If the particle is in an arbitrary orientation with respect to the incident beam, then oscillations will be excited in it in all three axis directions. If one looks perpendicularly at the body axis of the particle through a Nicol analyzer, one will see different color manifestations which depend on whether

*In a letter from Mr. Siedentopf, he was kind enough to call my attention to the importance of extending the theory to individually visible, i.e. submicroscopic, particles, whereas the particles treated here, which are small or microscopic compared to the wavelength, can not be made individually visible [sic].

the oscillation direction of the Nicol is parallel or perpendicular to the body axis, since different de-electrification coefficients P come into play for oscillations in these two directions.

If we use equation (6) to extract the values for P and P' from Table 3 and Table 5 for the axis ratio of a given meridian ellipse, we can then use equation (21a) to calculate the radiation from the particle for the various wavelengths, and thus the color for a given analyzer setting. This has been done in Table 7, in which the millimeter is the unit of length.

Table 7. The quantity F/V^2.

λ	$\frac{3}{4\pi}P=0$	0,2	0,4	0,5	0,6	0,8	1,0	1,1	1,2
420	9,68	10,56	10,38	9,89	9,22	7,65	6,12	5,45	4,84
450	7,82	8,51	8,29	7,84	7,27	5,92	4,70	4,17	3,68
500	5,47	7,70	7,51	11,07	11,48	10,24	7,74	6,54	5,50
525	5,48	8,97	10,47	18,91	21,64	19,28	11,98	9,15	7,07
550	5,77	10,87	15,49	36,54	46,59	30,17	13,30	9,22	6,68
600	7,20	18,94	46,93	160,7	77,31	17,00	6,70	4,73	3,53
650	9,73	41,90	186,3	53,71	21,20	6,68	3,20	2,40	1,86

λ	$\frac{3}{4\pi}P=1,25$	1,3	1,4	1,5	1,8	2,0	2,2	2,6	3,0
420	4,57	4,30	3,85	3,44	2,52	2,08	1,74	1,25	0,945
450	3,45	3,27	2,92	2,61	1,90	1,56	1,30	0,941	0,709
500	5,06	4,63	3,93	3,33	2,15	1,66	1,32	0,878	0,625
525	6,25	5,56	4,48	3,64	2,15	1,60	1,23	0,791	0,552
550	5,82	5,06	3,95	3,15	1,81	1,33	1,02	0,651	0,454
600	3,07	2,71	2,17	1,76	1,05	0,793	0,617	0,406	0,288
650	1,66	1,50	1,23	1,02	0,637	0,492	0,390	0,265	0,190

If, e.g., we are concerned with a prolate ellipsoid of rotation of axis ratio B/A = 0.57, then from Table 3, $(3/4\pi)P = 0.6$ and from equation 6, $(3/4\pi)P' = 1.2$. We thus obtain the color of the particle, if the oscillation direction of the analyzer is parallel to the body axis, from the sequence under the heading 0.6 in Table 7. If the Nicol is turned 90°, then the

sequence under the heading 1.2 determines the color. As can be seen, the radiation intensities in the two cases are completely different. With the first analyzer setting, the particle appears reddish yellow, and with the second, green.

The situation is similar with oblate particles. If the axis ratio of the ellipsoid is, e.g. B/A = 0.29, then from Table 5, $(3/4\pi)P' = 0.5$, and thus $(3/4\pi)P = 2$; the sequences underneath the headings corresponding to these numbers in Table 7 then give the colors for the two analyzer settings.

Since the numbers in Table 7 vary so strongly, their graphical representation is not convenient. Therefore, the radiation values have been given in Table 8 by setting the radiation for $\lambda = 525$ nm equal to unity, i.e., F/F_{525} has been tabulated.

Table 8. The quantity F/F_{525}.

λ	$\frac{3}{4\pi}P=0$	0,2	0,4	0,5	0,6	0,8	1,0	1,1	1,2
420	1,77	1,18	0,990	0,523	0,426	0,397	0,511	0,595	0,685
450	1,43	0,949	0,792	0,415	0,336	0,307	0,393	0,456	0,521
500	0,998	0,858	0,716	0,585	0,530	0,531	0,647	0,715	0,779
525	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
550	1,05	1,21	1,48	1,93	2,15	1,57	1,11	1,01	0,945
600	1,31	2,11	4,48	8,50	3,57	0,882	0,560	0,517	0,499
650	1,77	4,67	17,8	2,84	0,980	0,346	0,267	0,262	0,263

λ	$\frac{1}{4\pi}P=1,25$	1,3	1,4	1,5	1,8	2,0	2,2	2,6	3,0
420	0,731	0,773	0,860	0,947	1,17	1,30	1,41	1,58	1,71
450	0,552	0,589	0,651	0,717	0,885	0,978	1,06	1,19	1,28
500	0,810	0,833	0,879	0,915	1,00	1,04	1,07	1,11	1,13
525	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
550	0,930	0,910	0,883	0,867	0,843	0,833	0,828	0,823	0,822
600	0,492	0,489	0,485	0,485	0,491	0,497	0,503	0,513	0,521
650	0,266	0,271	0,274	0,280	0,297	0,308	0,317	0,335	0,344

The results for various values of $(3/4\pi)P$, indicated on the curves, have been plotted in Figures 5 and 6.

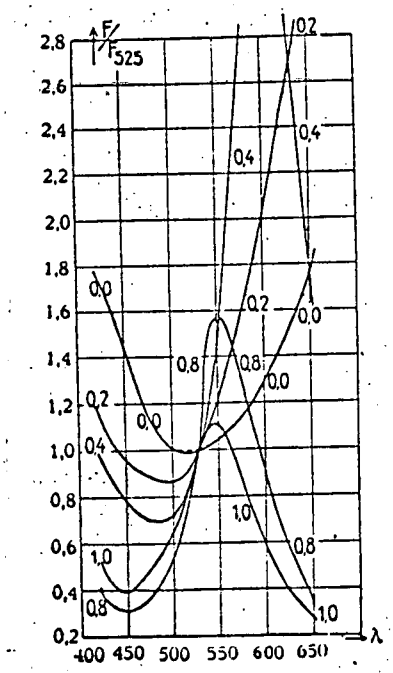

Fig. 5.

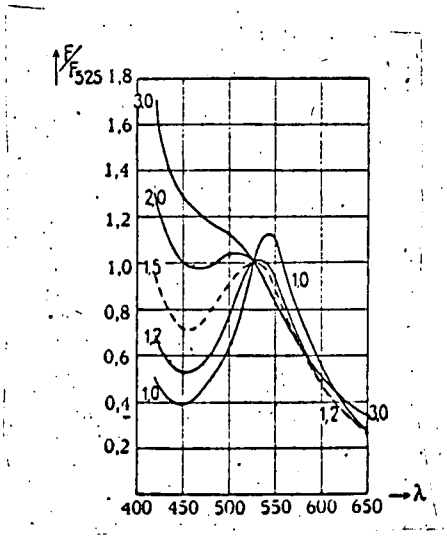

Fig. 6.

6. The Polarization

In order to study the polarization conditions of the light radiated laterally from the gold particles, we assume that a plane, linearly polarized wave propagates in the x-direction and that the oscillation direction of the electric vector forms angle δ with the y-axis.

Let the wave have amplitude 1 at point x = 0, so that it can be written in the form:

$$\begin{aligned} \mathfrak{E}_x &= 0, \\ \mathfrak{E}_y &= \cos\delta\, e^{2\pi i n t} \\ \mathfrak{E}_z &= \sin\delta\, e^{2\pi i n t} \end{aligned} \tag{22}$$

At this point let there be a particle in which, as before, we assume a coordinate system ξ, η, ζ whose ξ-axis coincides with the body axis.

Accordingly, we have

$$\begin{aligned}\mathfrak{E}_\xi &= \alpha_1 \mathfrak{E}_x + \alpha_2 \mathfrak{E}_y + \alpha_3 \mathfrak{E}_z \\ \mathfrak{E}_\eta &= \beta_1 \mathfrak{E}_x + \beta_2 \mathfrak{E}_y + \beta_3 \mathfrak{E}_z \\ \mathfrak{E}_\zeta &= \gamma_1 \mathfrak{E}_x + \gamma_2 \mathfrak{E}_y + \gamma_3 \mathfrak{E}_z\end{aligned} \tag{23}$$

By substitution of equation (22) in equation (23), we obtain

$$\begin{aligned}\mathfrak{E}_\xi &= e^{2\pi i n t}(\alpha_2 \cos\delta + \alpha_3 \sin\delta) \\ \mathfrak{E}_\eta &= e^{2\pi i n t}(\beta_2 \cos\delta + \beta_3 \sin\delta) \\ \mathfrak{E}_\zeta &= e^{2\pi i n t}(\gamma_2 \cos\delta + \gamma_3 \sin\delta)\end{aligned} \tag{24}$$

From equations (10) and (24), we then obtain f_ξ, f_η, and f_ζ, as follows:

$$\begin{array}{l|c|c|c} f_\xi = g\, e^{2\pi i n t}(\alpha_2 \cos\delta + \alpha_3 \sin\delta) & \alpha_1 & \alpha_2 & \alpha_3 \\ f_\eta = g'\, e^{2\pi i n t}(\beta_2 \cos\delta + \beta_3 \sin\delta) & \beta_1 & \beta_2 & \beta_3 \\ f_\zeta = g'\, e^{2\pi i n t}(\gamma_2 \cos\delta + \gamma_3 \sin\delta) & \gamma_1 & \gamma_2 & \gamma_3 \end{array} \tag{25}$$

If we now multiply by the coefficients from the columns alongside the equations and then add, using the relations for the direction cosines, and if we also write the complex quantities g and g' in the form

$$g = m_0^2 \frac{3}{4\pi} V l e^{-i\psi}, \quad g' = m_0^2 \frac{3}{4\pi} V l' e^{-i\psi'} \tag{26}$$

then we obtain

$$\begin{aligned} f_x &= m_0^2 \frac{3}{4\pi} V[l\cos(2\pi n t - \psi) - l'\cos(2\pi n t - \psi')] \\ &\quad \alpha_1(\alpha_2 \cos\delta + \alpha_3 \sin\delta) \\ f_y &= m_0^2 \frac{3}{4\pi} V[l\cos(2\pi n t - \psi) - l'\cos(2\pi n t - \psi')] \\ &\quad \alpha_2(\alpha_2 \cos\delta + \alpha_3 \sin\delta) + m_0^2 \frac{3}{4\pi} V l' \cos(2\pi n t - \psi')\cos\delta \\ f_z &= m_0^2 \frac{3}{4\pi} V[l\cos 2\pi n t - \psi) - l'\cos(2\pi n t - \psi')] \\ &\quad \alpha_3(\alpha_2 \cos\delta + \alpha_3 \sin\delta) + m_0^2 \frac{3}{4\pi} V l' \cos(2\pi n t - \psi')\sin\delta \end{aligned} \tag{27}$$

Now let us imagine an observer looking along the y-direction, i.e. perpendicular to the incident beam; let him be looking through a Nicol whose oscillation direction makes the angle ε with the x-axis, and through a Babinet compensator which imparts a phase lag β to the x-component relative to the z-component.

For this observer, f_y is completely out of the question, since a dipole is not radiating along the direction of his axis; for f_x and f_z, only the sum of the components which fall in the oscillation direction of the analyzer, i.e. $f_x\cos\varepsilon + f_z\sin\varepsilon$, can be taken into account. This sum, however, is known after the phase lag β of the Babinet compensator has been applied to f_x.

The square of these components of f is proportional to the intensity of that portion of the light scattered by the particle under observation which is perceivable by the observer.

First we take a time average of the expression obtained thus; then, in order to treat natural incident light, we give δ all possible values and calculate their mean value. Finally, we also give α_1, α_2, and α_3 all possible values, by setting up the relations

$$\alpha_1 = \cos\vartheta, \quad \alpha_2 = \sin\vartheta\cos\varphi, \quad \alpha_3 = \sin\vartheta\sin\varphi \tag{28}$$

This gives the correct result, for since the particles lie at random, the amplitudes are not additive, but rather the intensities of the light oscillations of each individual particle. It is likewise correct to assign all possible values to δ in the expression for the square of the moment, since the linearly polarized light of various azimuths, which is contained in naturally incident light, is incoherent.

If we also assume that the particles deviate only slightly from the spherical shape, so that $\zeta' - \zeta$ and $\psi' - \psi$ are small quantities, we then find that the intensity of the light transmitted by the analyzer is given by

$$J \sim \sin^2\zeta + Q \tag{29}$$

(We use the proportionality [sic] symbol since a common factor for the two terms has been left out.)

Expression (29) is completely independent of the phase lag β of the Babinet compensator, i.e. there is -- in agreement with observation -- no elliptically polarized light present.

The first term on the right side represents linearly polarized light whose oscillation direction is parallel to the z-axis, thus perpendicular to the plane through the incident beam and the direction of vision. The second term Q represents natural light.

From Steubing's observations we thus find, in fact, that along with the linearly polarized light expected on the basis of Mie's theory, there was always a small amount of natural light present. We can thus conclude with certainty that an exactly spherical shape for the particles is out of the question.

If we compare the absorption and polarization observations with the theory, we find from the former that the deviations from spherical shape can not be large, and from the latter that small deviations, however, must be present.

The quantity Q, which gives the intensity ratio of the natural to the linearly polarized laterally radiated light, has the value

$$Q = \frac{2}{15}\,\frac{l^2 + l'^2 - 2\,l\,l'\cos(\psi - \psi')}{l'^2} \tag{30}$$

where

$$\overline{l\,e^{-i\psi}} = \frac{m'^2 - 1}{3 + (m'^2 - 1)\,\frac{3}{4\pi}\,P}, \quad \overline{l'\,e^{-i\psi'}} = \frac{m'^2 - 1}{3 + (m'^2 - 1)\,\frac{3}{4\pi}\,P'} \tag{31}$$

1 - Q is thus the so-called degree of polarization.

Since the deviation from spherical shape has been assumed to be small, we can write, for prolate ellipsoids of rotation:

$$\frac{3}{4\pi}P = 1 - \frac{4}{5}\,\frac{A-B}{A}, \quad \frac{3}{4\pi}P' = 1 + \frac{2}{5}\,\frac{A-B}{A}$$

and for oblate ellipsoids of rotation:

$$\frac{3}{4\pi}P = 1 + \frac{4}{5}\,\frac{A-B}{A}, \quad \frac{3}{4\pi}P' = 1 - \frac{2}{5}\,\frac{A-B}{A}$$

In both cases, we obtain

$$Q = 0{,}192\left|\frac{m'^2 - 1}{m'^2 + 2}\right|^2\left(\frac{A-B}{A}\right)^2 = h\left(\frac{A-B}{A}\right)^2 \tag{32}$$

In the following table, h has been calculated by means of the values given by Mie[9] for $\left|\frac{m'^2-1}{m'^2+2}\right|^2$:

Table 9.

λ	$\left\|\frac{m'^2-1}{m'^2+2}\right\|^2$	h
420	0,790	0,152
450	0,805	0,154
500	2,05	0,394
525	3,84	0,737
550	5,18	0,995
600	3,70	0,710
650	2,42	0,465

If we allow incident linearly polarized, non-natural light whose oscillation direction is parallel to the z-axis, i.e. perpendicular to the plane through the incident beam and the direction of vision, then $\delta = \pi/2$ must be inserted in equation (27). Other than that, the calculation is completely analogous, and instead of Expression (29), we obtain

$$J \sim \sin^2\zeta + Q'$$

where

$$Q' = 0{,}096 \left|\frac{m'^2-1}{m'^2+i^2}\right|^2 \left(\frac{A-B}{A}\right)^2 = \frac{h}{2}\left(\frac{A-B}{A}\right)^2 \qquad (33)$$

in other words, half of the amount for the relative contribution of natural light.

Unfortunately, I could find no quantitative data on the degree of polarization, from which one could draw a conclusion regarding the deviation from spherical shape.**

The calculations in the present study should also be carried out for silver particles in order to see whether one can derive information on their shape in the colloidal state, from their color.

Strassburg, 15 January 1912.

** Mr. Steubing was kind enough to inform me in a letter that for incident natural light, the non-polarized portion of the laterally scattered light represents less than 1% of the polarized portion. If we apply this result to λ = 550 nm, it then follows from equation (32) and Table 9 that B/A > 0.9 applied in any case, i.e. that the particles deviated less from the spherical shape than the ellipsoid drawn in Figure 1, No. 2.

Submitted on 16 January 1912.

References

[1] Mie, G., *Ann. d. Phys.*, 25, 377 (1908).

[2] Steubing, W., Dissertation, Greifswald, 1908.

[3] Cf. Figure 25 on p. 438 of Mie's treatise.

[4] Lord Rayleigh, *Phil. Mag.*, 44, 28 (1897).

[5] Cf., e.g., R. Gans, "Electrostatics and Magnetostatics," *Mathematical Encyclopedia*, 5, Article 15, § 16, p. 329.

[6] Cf., e.g., R. Gans and H. Happel, *Ann. d. Phys.*, 29, 280 (1909), equations 4 and 5.

[7] Cf. G. Mie, loc. cit., p. 436, equation 98; or R. Gans and H. Happel, loc. cit., p. 294, equation 50.

[8] Siedentopf, H. and R. Zsigmondy, *Ann. d. Phys.*, 10, 1 (1903).

[9] loc. cit., p. 418.

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